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Disposal, Recycle, and Utilization of Modified Fly Ash from Hydrated Lime Injection into Coal-Fired Utility Boilers

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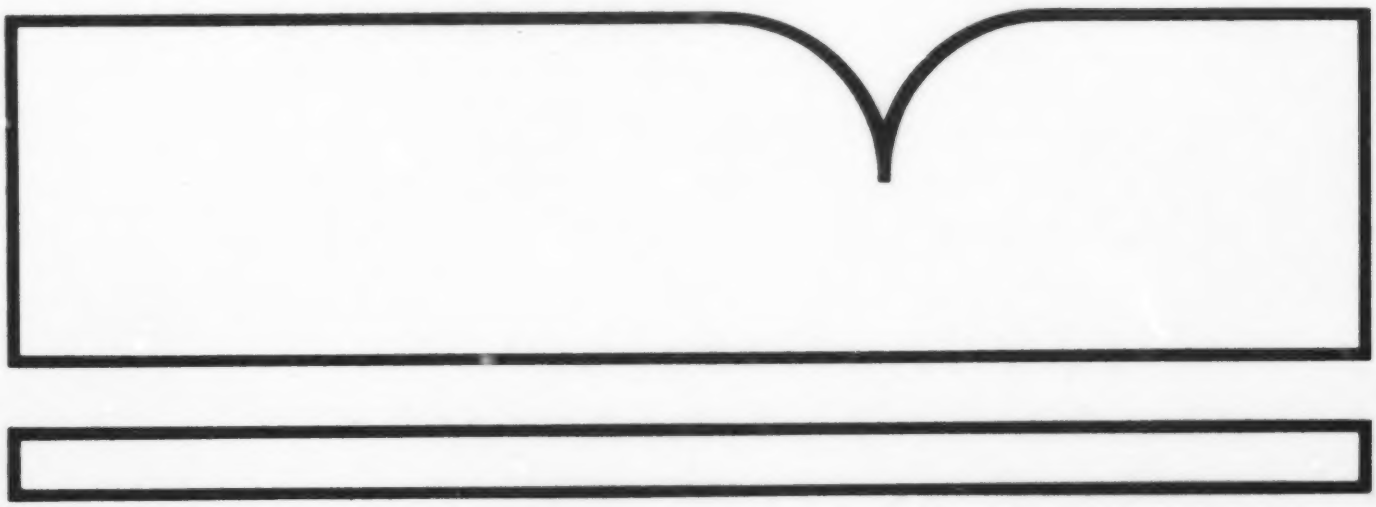

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16. ABSTRACT The paper gives results of an assessment of the disposal, utilization, and recycle of a modified fly ash from the injection of hydrated lime into a coal-fired utility boiler. The process, developed as a low-cost alternative for achieving moderate degrees of SO2 control at coal-fired power plants, is being demonstrated in a 105-MW, coal-fired utility boiler at the Edgewater Station of Ohio Edison Company. Both the laboratory tests and the large-scale disposal study showed that the modified ash can be safely handled and landfilled. The studies showed that the cementitious reactions within the wetted ash can produce a nearly impermeable material, if the ash is properly conditioned and placed. One of the most promising utilization concepts appears to be synthetic aggregate production for bituminous pavement applications. One of the most promising recycle concepts appears to be the use of coarse limestone injection with cyclonic removal of the coarse calcine particles followed by hydration and reinjection. This effectively yields the performance of hydrated lime at the cost of coarse limestone, which is much less expensive.

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INTRODUCTION

This paper presents an assessment of the disposal, utilization, and recycle of a modified fly ash from the injection of hydrated lime into a coal-fired utility boiler. The hydrated lime injection process is being developed by the US Environmental Protection Agency (EPA) as a low-cost alternative for achieving moderate degrees of SO_2 control at coal-fired power plants. In this process, hydrated lime is injected into the upper furnace where the flue gas temperature is about 2200°F (1200°C). The hydrated lime decomposes, and the resulting quicklime, CaO, captures SO_2 according to:

$$Ca(OH)_2 \text{ ---> } CaO + H_2O \quad (1)$$

$$CaO + SO_2 + 1/2O_2 \text{ ---> } CaSO_4 \quad (2)$$

Since only 25 to 30% of the CaO is converted to $CaSO_4$ on a molar basis, the waste product contains a substantial amount of free lime, CaO, in addition to the calcium sulfate product, $CaSO_4$. These materials are ultimately collected along with the coal fly ash in an electrostatic precipitator (ESP) or a fabric filter (FF). The resultant waste product is a modified fly ash consisting of a mixture of fly ash, free lime, and calcium sulfate. Some of the lime reacts with fly ash components in the boiler, forming calcium aluminosilicates in a manner analogous to the lime/clay reactions in cement kilns. This causes the modified fly ash to have cement-like hardening characteristics when mixed with water.

The US EPA, the State of Ohio, and Babcock & Wilcox are demonstrating the hydrated lime injection process in a 105-MW, coal-fired utility boiler at the Edgewater Station of Ohio Edison Company (OEC). The plans for the 14-mo demonstration program have been reported by Hendriks and Nolan (1). Proper management of the waste product has been an area of interest for both EPA and OEC. In response, the US EPA has been conducting an extensive research program through its contractor, Southern Research Institute (SoRI). The goal of the program is to support the demonstration program's needs for safe ash handling and disposal, while also conducting long-range research on the utilization and recycle of the modified fly ash.

OBJECTIVES AND SCOPE

The objectives of the waste management research program are: (1) to characterize the modified fly ash that results from the hydrated lime injection process; (2) to identify potential problems with landfill disposal and suggest solutions; (3) to develop processes for utilization of the modified fly ash as a salable by-product; and (4) to develop processes for recovery and recycle of the unused lime in the modified fly ash. Objectives 1 and 2 apply directly to the Edgewater Demonstration Project as well as the generic hydrated lime or limestone injection process. Objectives 3 and 4 are primarily directed toward long-range optimization of the process and improvement of process economics.

The results of this research program are being used to develop guidelines for management of modified fly ash from both a generic process and the Edgewater Demonstration. These guidelines will include: (1) recommendations for proper conditioning, transport, and placement of the waste; (2) monitoring and neutralization procedures to control alkaline runoff; and (3) sampling and testing procedures to ensure adequate stabilization and low permeabilities. An extensive program of laboratory and large-scale testing has been conducted to provide the basis for these guidelines.

Literature reviews, industrial contacts, and laboratory testing have been used to identify promising concepts for utilization of the modified ash. One of the most promising concepts, synthetic aggregate production, has been tested in the laboratory and in pilot equipment to demonstrate its technical feasibility. The properties of the aggregate product are being evaluated to demonstrate its acceptability in asphalt pavement applications.

Pilot combustor tests have shown that the modified ash can be hydrated and reinjected into the furnace for additional SO_2 removal. Further research is focusing on the separation of the fly ash and lime components, so that the recycle process will not produce excessive particulate loadings in the boiler or particulate collector.

The work described in this paper was performed prior to start-up of the Edgewater Demonstration, which is the first full-scale application of hydrated lime injection in the United States. For the laboratory testing it was therefore necessary to use modified fly ash generated in a 1×10^6 Btu/hr (1.06 GJ/hr) combustor designed to simulate the temperature profile in a full-scale utility boiler. The design and operation of this combustor have been described elsewhere (2). Extensive testing was done to show that the combustor-produced ash was similar to that produced in a full-scale boiler (3,4). The modified ash was generated using the Pittsburgh No. 8 coal and the calcitic hydrated lime targeted for use at the Edgewater Demonstration.

For large-scale tests of ash conditioning, transport, and placement, the pilot combustor could not provide an adequate quantity of modified ash. For these tests, several truckloads (about 84 tons or 76 MT) of modified fly ash were obtained from full-scale tests of hydrated lime injection at Ontario Hydro's Lakeview Station (5).

LANDFILL DISPOSAL OF MODIFIED FLY ASH

Laboratory Evaluation of Ash Characteristics

In order to evaluate the suitability of modified fly ash for landfill disposal, samples of the modified ash produced in the pilot combustor were characterized by the following procedures: (1) chemical analysis, (2) leachate pH and metals analysis, (3) permeability measurements, (4) temperature-rise studies, and (5) wetting tests. All of these tests were performed on ash generated from the hydrated lime and Pittsburgh No. 8 coal targeted for use

at the Edgewater Demonstration. The procedures used in these tests have been described in a previous paper (6).

Table I gives a representative chemical analysis of the modified ash. Assuming that all of the sulfur is associated with $CaSO_4$, this analysis translates into a composition of 29% free lime (CaO), 37% $CaSO_4$, and 34% coal fly ash by weight, corresponding to a molar calcium utilization of 34%. This is only slightly higher than the 25 to 30% utilizations typically obtained with hydrated lime injection (7).

Table II gives data on pH and the Resource Conservation and Recovery Act (RCRA) metals content of leachates generated by the Extraction Procedure (EP) Toxicity Test (8). The levels of all eight priority metals (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag) are well below RCRA standards. Based on these results, it appears unlikely that the modified ash could be classified as a hazardous waste based on EP Toxicity. This is as expected since these metals are insoluble at high pH. Actually, As and Se can be soluble in their anionic forms (arsenate and selenate), but this was not suggested by the leachate analyses. The high pH of these leachates may indicate potential problems with alkaline runoff from the landfill site. Any discharged runoff must be within National Pollutant Discharge Elimination System (NPDES) pH limits of 6 to 9.

To investigate the potential seepage of leachates through the ash and into groundwater, permeability measurements were performed on samples of modified ash that were mixed with water and cured in the laboratory. The wetted ash was placed in a cylindrical mold, hand tamped, and allowed to cure for 30 days prior to testing in a falling-head permeameter (9). As shown in Table III, the permeability can approach that of a clay liner (1×10^{-7} cm/sec) after a 30-day cure. Such a low level of permeability coupled with the low metal concentrations would effectively minimize the potential for groundwater contamination by leachates.

Since wetting of the ash is necessary to control fugitive dust and promote stabilization, there is concern about the highly exothermic reaction of the water with the free lime in the ash, and whether this could lead to classification as a reactive waste under RCRA regulations. This effect was quantified by temperature-rise studies performed by the ASTM slaking test (10) and tests designed to simulate wetting in the Edgewater ash conditioning system. The latter tests were done in both a 1-ft^3 (28.3-L) ribbon blender and a 4.5-qt (4.25-L) KitchenAid mixer. These tests have been described in detail in a previous paper (6). The results, which are summarized in Table IV, show that the temperature rise is maximum at a water-to-lime molar ratio of 1:1. At lower ratios, there is an insufficient amount of water to react with the free lime. At higher ratios, the excess water absorbs the heat of reaction and cools the ash. At ratios higher than 7:1, the wetted ash became mud-like and sticky. Based on these results, the optimum water-to-lime ratio appeared to be between 3:1 and 7:1. For the Edgewater Demonstration ash, this would correspond to the addition of 29 to 67% water, expressed as a percentage of the weight of dry modified ash. For comparison, 5 to 10% water is typically used to control dusting with ordinary fly ash.

Large-Scale Study of Ash Conditioning and Disposal

A large-scale study of ash conditioning and disposal was conducted using 84 tons (76 MT) of modified fly ash obtained from hydrated lime injection tests at Ontario Hydro's Lakeview Station. Pneumatic trucks were used to transport the ash from the Lakeview Station to the Edgewater Station of Ohio Edison, where the study was conducted. Grab samples taken from the trucks showed an average free lime (CaO) content of 24%, which was slightly lower than that of the modified ash produced in the pilot combustor for the laboratory tests.

The Lakeview ash was pneumatically loaded into the Edgewater Unit 3 ash silo from which it was discharged through an unmodified Dravo-Wellman conditioning system into open dump trucks. In the Dravo-Wellman system, the ash was wetted using four sets of overhead spray nozzles while being conveyed in a twin-screw mixer similar to a pug mill. The flow of ash from the silo into the conditioning system was controlled by a gate valve and star feeder. Water addition rates were controlled using a rotameter.

The wetted ash was discharged from the conditioning system into open dump trucks and hauled to a prepared landfill test site. This procedure was carried out in 10 different batches, corresponding to 10 different truck loads of wetted ash. The water addition rate was adjusted between batches so that the effect of different water-to-lime ratios could be ascertained.

The optimum water-to-lime molar ratio was projected to be about 5:1 based on the previous laboratory wetting tests. For the large-scale study, it was decided to vary the water-to-lime ratio around this optimum value. The target values were 3.5:1, 4.5:1, 5.5:1, and 5.0:1, with some runs done according to normal plant practice (visual assessment of the degree of wetting). These target ratios were based on acid-base titration of the dry ash where the alkalinity found within 20 min was ascribed to CaO. Subsequently, SoRI's analyses of digested samples showed that the actual water-to-lime ratios were 2.5:1, 3.2:1, 3.9:1, and 3.6:1. These four mixtures were placed in four separate piles within the landfill test site. The remaining six piles consisted of the following: a preliminary trial run (Run No. 1), a non-uniform sludge produced when the pug mill tripped out (Run No. 5), and four batches (Run Nos. 7-10) produced using normal plant conditioning practice, a condition expected to occur periodically.

At the lowest water-to-lime ratio (2.5:1), considerable steam was evolved from the wetted ash, and small, volcanic-type eruptions were observed in the truck beds. At the higher ratios, the degree of steaming was greatly reduced, and no eruptions were noted. Temperatures within the wetted ash in the truck beds varied from 190 to 209°F (88 to 98°C) depending on water-to-lime ratio and location. The sides of the truck bed were hot to the touch.

After allowing a minimum of 15 min for the steaming to subside, the truck beds were covered with tarps, and the wetted ash was hauled to the landfill test site for placement. The test site covered an area of approximately 40 by 60 ft (12 by 18 m) and was surrounded by a lined perimeter trench that

drained into a lined catch basin (sump). The wetted ash was placed in separate piles as indicated in Figure 1. Each pile was leveled and compacted with a backhoe and Vibra-Tamps.

Samples of the runoff from the landfill test cell were collected by Ohio Edison personnel for analysis of pH, alkalinity, solids content, and RCRA metals (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag). Samples were taken from the catch basin (sump) and the perimeter trench at the locations indicated by circles in Figure 1. The results obtained over a 23-day period are summarized in Table V. The pH in the sump varied only slightly from 6.8 to 7.7, while the suspended solids in the sump varied from 5 to 26 ppm. Both parameters were within NPDES discharge limits (pH between 6 and 9, and monthly average suspended solids below 30 ppm). Suspended solids concentrations were much higher in the trench than in the sump, indicating that a substantial degree of settling occurred in the sump. The pH levels were initially high in the trench samples (11.4 to 12.0 in first 5 days). These pH levels fell to near 7, however, after a few days. It is assumed that chemical reactions in the ash stabilized the mixture, reducing the free alkalinity. Carbonation by atmospheric CO_2 could also have been a contributing factor.

As expected from the laboratory tests, the runoff analyses show very low levels of the RCRA metals, which are generally insoluble under alkaline conditions. In this respect, the modified ash is preferred over the same ash produced without lime injection. Nevertheless, it appears that the runoff should be contained and directed to a monitored sump before discharge. If necessary, acid neutralization or carbonation could be employed to reduce the pH prior to discharge of any runoff water.

To investigate the hardening characteristics of the landfilled ash and the potential for groundwater contamination, permeability measurements were made on core samples from the various ash piles. The core samples were obtained using standard concrete core drilling equipment and tested by the falling head test method (9). As shown in Figure 2, the permeability of the wetted ash decreased as the water-to-lime ratio increased. The lowest average permeability, about 2×10^{-6} cm/sec, was obtained with the hardened sludge produced when the pug mill tripped out. This suggests that the optimum water-to-lime ratio is even higher than the maximum tested, from the point of view of permeability. Higher rates of water addition could yield results comparable to a clay liner (1×10^{-7} cm/sec). When coupled with the low levels of metals in the leachate, the potential for groundwater contamination should be minimal.

UTILIZATION OF MODIFIED FLY ASH

The principal compounds found in modified fly ash are calcium oxide, calcium sulfate, and pozzolanic fly ash. Ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$], a desired compound which is primarily responsible for cementitious properties, is formed upon wetting and curing modified fly ash specimens. The cementitious properties of the modified fly ash make it an attractive starting material for construction aggregate. The use of this aggregate in road construction materials, structural fill, soil stabilization, asphalt admixture, and roofing materials is being investigated. Laboratory studies are being performed at

SoRI; Industrial Resource Development, Inc. (IRD), of Devon, Pennsylvania; and Aardelite Holding B.V. (Aardelite) of Nunspeet, The Netherlands, to determine the feasibility of producing synthetic aggregate from modified fly ash. Modified fly ash has been mixed with various amounts of water, pelletized, and cured using different curing techniques for evaluation of aggregate properties. IRD, Aardelite, and SoRI have prepared and continue to test these aggregates for construction applications. The free lime content of the modified fly ash has also prompted other areas of interest, including use in FGD scrubber feed, scrubber sludge stabilization, acidic waste neutralization, and metal waste stabilization. These areas have not yet been investigated.

IRD Synthetic Aggregate Evaluations

IRD used the modified fly ash prepared from the Pittsburgh No. 8 coal and hydrated lime to make cured specimens (pellets) for evaluation. The chemical analysis of the modified fly ash was given previously in Table I.

Pellets were produced from the modified fly ash and the amount of water required to give optimum (maximum) density (43% by weight of wetted ash). This moisture content corresponds to a water-to-free lime ratio of 8:1. The mixture was pressed into cylinders and cured in a room-temperature, humidified atmosphere. Compressive strengths of 1870 to 2506 psi (12.9 to 17.3 MPa) were measured after 50 days. X-Ray diffraction showed 18% ettringite in the cured sample. This ettringite content was estimated by comparison to previous X-ray diffraction data on concrete samples containing known amounts of ettringite. This level of ettringite suggests a moderate degree of cementitious activity.

The pellets were crushed to produce a size-graded (1/2-in. to No. 16 sieve or 12.7- to 1.19-mm) aggregate. The appearance of the size-graded aggregate resembled crushed limestone. The Mohs hardness showed a range of 4 to 6, which is normally found in high-quality limestone. This aggregate had a density of 97.9 to 147.8 lb/ft^3 (1.57 to 2.37 g/cc) and a water absorption of 23%. It is likely that the commercial aggregate would be made using a vacuum extrusion process, which would probably increase the density and decrease the water absorption of the aggregate.

When mixed with asphalt, the size-graded aggregate was thoroughly coated and produced a mixture that appeared suitable for paving material. The asphalt absorption was 7% by weight, which is somewhat higher than the typical 5%. However, the amount of asphalt consumed should decrease when using a commercial vacuum extrusion process.

Aardelite Synthetic Aggregate Evaluations

Aardelite performed preliminary bench-scale evaluations on aggregate made using the modified fly ash from the Pittsburgh No. 8 coal and hydrated lime (see Table I for chemical analysis). The modified fly ash was mixed with water in the proportions of 80% modified fly ash and 20% water by weight (80/20 mix), pressed into cylinders using a pressure of 1400 to 7000 psi (9.6 to 48.2 MPa), and steam cured for 12 to 16 hr. The density of the cylinders ranged from

82.3 to 97.9 lb/ft^3 (1.32 to 1.57 g/cc), and compressive strengths of 1876 to 4533 psi (12.9 to 31.2 MPa) were obtained. This compares to 3000 psi (20.7 MPa) required for good road aggregate. It is known that pellets with compressive strengths of over 3000 psi (20.7 MPa) will produce good quality aggregate in Aardelite's factory operation. These results suggested that the modified fly ash was suitable for Aardelite's rotary pelletizing process. This prompted the need for a larger quantity of modified fly ash to be used in a pilot study.

A larger quantity of modified fly ash (approximately 14 tons or 13 MT) was obtained from a co-generating heating facility in Malmo, Sweden. Table I gives the chemical analysis of the ash. This facility started up in February 1986 with the goal of achieving 50% SO_2 removal. The modified fly ash was obtained during hydrated lime injection tests at a calcium-to-sulfur ratio of 2.22. The coal used was a Polish coal with a sulfur content of 0.63% and an ash content of 8.6%.

To determine the best ash mixture for the pilot study, bench-scale evaluations were performed on different mixtures of modified fly ash. These mixtures were pressed into cylinders (using 2310 psi or 15.9 MPa) and steam cured. The compressive strength was about 10,780 psi (74.3 MPa) for the mixture made from the 80/20 mix. The different mixtures and compressive strengths are shown in Table VI. The sulfur content of the mixtures ranged from 2.2 to 6.0%. The high sulfur content makes the aggregate unacceptable for concrete applications due to the retarding effect of calcium sulfate on the setup of the cement. Therefore, aggregate testing was directed toward highway pavement applications.

SoRI's Synthetic Aggregate Evaluation

Different mixtures, hydration times, curing techniques, and curing times were examined in the laboratory. Compressive strengths were used to determine promising procedures. The modified fly ash made from the Pittsburgh No. 8 coal and hydrated lime was used in these studies (chemical analysis given in Table I).

The weight percent ratios ranged from 90/10 to 75/25 modified fly ash/water mixtures. The mixtures were allowed to hydrate for different periods of time before being pressed into cylinders. The hydrated material was then placed in a die and pressed at a pressure of 3000 psi (20.7 MPa) in a Carver hydraulic laboratory press. The cylindrical pellets were removed and cured using different curing techniques. The curing techniques that were investigated included: room-temperature humidified cure, atmospheric steam cure, autoclave cure, and CO_2 cure. After different cure times, the compressive strength was determined using a Tinius-Olsen universal testing machine.

The room-temperature, humidified atmosphere was kept at a relative humidity of 95 ± 5%. The most promising pellet from the room temperature humidified cure was an 80/20 mix with a 10-min hydration time and a 40-day cure in the room-temperature humidified chamber. This pellet had a compressive strength of 4223 psi (29.1 MPa).

Pellets were also placed in an atmospheric steam cure for 6 to 12 hr before being placed in a room-temperature, humidified chamber. The most promising pellet from this curing technique had a compressive strength of 3512 psi (24.2 MPa). This pellet was an 80/20 mix with a 5-min hydration time, 12-hr steam cure, and was placed in the room-temperature humidified chamber for 50 days.

The autoclave cure was performed in a Boekel Industries autoclave using steam at 80 psi (551 kPa) and 312°F (156°C). The pellets were autoclave cured and then placed in a room-temperature, humidified chamber. The most promising compressive strength was 1573 psi (10.8 MPa). This pellet was made from an 80/20 mix with a 10-min hydration time, 15.5-hr autoclave cure, and was placed in a room-temperature humidified chamber for 9 hr.

Literature suggested that curing building materials in an atmosphere enriched in CO_2 causes an increase in strength at shorter curing times (11). To examine this, pellets were made and cured in a CO_2 atmosphere before being placed in a room-temperature humidified chamber. The most promising pellet from this curing technique had a compressive strength of 5778 psi (39.8 MPa). This pellet was an 80/20 mix with 12-min hydration time, 30-hr CO_2 cure, and was placed in a room-temperature humidified chamber for 24 hr. This is very encouraging since strengths of over 5000 psi (34.4 MPa) can be developed in 2 days. The gain in strength is attributed to the reaction of $Ca(OH)_2$ with CO_2 according to:

$$Ca(OH)_2(s) + CO_2(g) \text{ ---> } CaCO_3(s) + H_2O(l) + \text{heat} \qquad (3)$$

SoRI performed the EP Toxicity Test on aggregates from IRD, pellets from Aardelite and SoRI, and an asphalt mixture containing the aggregate from IRD. Table VII shows that the metal concentrations in the leachates were all well below the RCRA allowable limits.

Summary of the Synthetic Aggregate Study

The most promising curing technique appears to be the CO_2 cure, in which compressive strengths of over 5000 psi (34.5 MPa) were developed in 2 days of curing. However, the economic feasibility of the process must be determined. The steam curing technique, with compressive strengths of 4300 to 4500 psi (29.6 to 31.0 MPa) obtained by the Aardelite process, is also very promising and may be more economically feasible than the CO_2 cure.

IRD has obtained compressive strengths of 1870 to 2506 psi (12.9 to 17.3 MPa) with an optimum moisture content of 43% to produce a pellet with an optimum density and high compressive strength. However, work performed by SoRI, using the same procedure as IRD, has shown that compressive strengths of 4223 psi (29.1 MPa) can be obtained with an 80/20 mix. These results indicate that the water content required to yield maximum density does not necessarily yield maximum compressive strength.

The EP Toxicity Test shows that aggregates from IRD, pellets from Aardelite and SoRI, and an asphalt mixture containing the aggregate from IRD are not subject to leaching of toxic trace metals.

Since the modified fly ash aggregates have a high sulfur content, making the aggregate unacceptable for concrete applications, emphasis has been directed toward using the aggregate in road applications. This aggregate will be tested in accordance with the Ohio Department of Transportation (ODOT) specifications. The soundness (weight loss in sodium sulfate solution) test (specification of 12%) and the Los Angeles (LA) abrasion (weight loss by abrasion) test (specification of 40%) will be used to screen the aggregate. The asphalt containing aggregate must pass the ODOT specifications for Marshall test (determination of amount of asphalt required by aggregate), freeze/thaw test (stress on asphalt/aggregate mixture caused by freezing and thawing), and gradation test (sieve size analysis)(12).

Modified fly ash aggregates are also being considered for use in the roofing industry. Aggregate made from modified fly ash may be used as a substitute for headlap (used on the top half and back of the shingle for thickness). Headlap currently sells for over $30/ton. Tests to be performed on the roofing aggregate include: leaching and discoloration of the aggregate when wet, water absorption, asphalt absorption, pH, adhesion, shatter upon cutting, granular color, and sieve size.

RECOVERY AND RECYCLE OF UNUSED SORBENT

As mentioned previously, only 25 to 30% of the calcium is utilized (i.e., converted to $CaSO_4$) in the hydrated lime injection process. This means that 70 to 75% of the sorbent calcium content is discarded in the waste product without being used. If this unused sorbent were recovered and recycled, the calcium utilization would be improved, the amount of waste product would be reduced, and less fresh sorbent would be required. These effects would translate into substantial cost savings, making the process more economically attractive. Thus, there is considerable incentive to develop processes for recovery and recycle of unused sorbent.

Review of Previous Work on Recovery and Recycle

In a previous paper (6), we reviewed work done at Argonne National Laboratory (13) which showed that modified fly ash from fluidized-bed combustors could be hydrated and reinjected to achieve additional utilization of the sorbent's calcium content. This encouraged research on the hydration and recycle of the modified ash from hydrated lime injection into the SoRI pilot combustor. Samples of modified ash were first hydrated in the laboratory. Thermogravimetric analyses (TGA) showed that much of the free lime content was converted to $Ca(OH)_2$, and nitrogen adsorption studies showed that the specific surface area of the ash was increased by 35 to 57%. These results suggested that hydration could be used to reactivate the modified ash for additional SO_2 capture.

The encouraging results obtained in the laboratory prompted a recycle test in the pilot combustor. A large quantity of previously generated ash was hydrated in a cement mixer using 60% excess water (to allow for steam loss). About 97% of the free lime content was converted to $Ca(OH)_2$, and the specific surface area was doubled. The hydrated ash was injected back into the pilot combustor at a flue gas temperature of about 2200°F (1200°C). The injection rate was adjusted to yield predetermined ratios of available calcium-to-sulfur, where only the calcium that was not already sulfated was considered to be available. At a ratio of 2:1, the sulfur capture was 51%, corresponding to a molar calcium utilization of about 25%. Thus, the performance of the recycled ash was essentially equivalent to that of commercial hydrated lime, when compared on the basis of equivalent unreacted calcium.

Ash/Sorbent Separation Techniques

While the recycle tests were very encouraging, it was realized that excessive particulate loadings would result if the coal fly ash were recycled along with the sorbent material. If a significant fraction of the sorbent were to be recycled, it was apparent that it would have to be separated from the coal fly ash. At this point, the recycle research effort was focused on the development of ash/sorbent separation techniques.

In our previous paper (6), we reviewed several potential separation techniques, including: (1) use of the ESP as a separator, (2) inertial separation, (3) magnetic separation, (4) froth flotation, and (5) steam hydration/elutriation. Magnetic separation was found to be very ash-specific and environmentally unacceptable due to the high-pH wastewater generated. No significant degree of ash/sorbent separation was achieved with froth flotation, apparently due to the very fine particle sizes and high pH. The other techniques appear to be feasible if there is sufficient difference between the fly ash and sorbent particles sizes. This can be exploited, for example, by collecting the large particles in the inlet fields of an ESP, while collecting the smaller particles in the outlet fields.

With hydrated lime injection, the sorbent particles typically have a mass median diameter (mmd) of 2 to 5 μm, while the coal fly ash particles have an mmd of 15 to 20 μm. This difference in particle size may be sufficient to allow some degree of separation in an ESP, with the inlet fields collecting mostly fly ash, and the outlet fields collecting mostly sorbent. This concept has not been tested due to the lack of a multi-field ESP to use with the pilot combustor. The Edgewater Demonstration will provide an opportunity to evaluate the degree of separation obtained in a highly efficient, six-field ESP. It may even be possible to reduce the power supplied to the inlet fields to increase the particle sizes collected and thereby enhance the degree of separation.

Coarse Limestone Injection with Cyclonic Sorbent Recovery

Inertial separation of ash/sorbent mixtures from hydrated lime injection would require a cyclone or mechanical collector with an aerodynamic cutpoint between 5 and 15 μm, based on the mmds given previously. While this can be

achieved in the laboratory (e.g., in a Bahco classifier), it may require an unacceptably high pressure drop in a power plant with limited fan capacity. The pressure drop requirement could be reduced by using a cyclone with a larger cutpoint and replacing the hydrated lime with a coarse sorbent (e.g., a coarse limestone). The coarse limestone would be poorly utilized in its first pass through the boiler, but it would be easily separated from the fly ash in a cyclone or mechanical collector. The separated sorbent could then be hydrated and reinjected without the penalty of accompanying fly ash. In this manner, it may be possible to achieve the performance of hydrated lime at the cost of coarse limestone, which is much less expensive.

The coarse limestone recycle concept is now being evaluated in the SoRI pilot combustion system. Tests are being conducted with a 14 by 120 mesh (1410 by 125 μm) limestone obtained from the Tenn-Luttrell Lime Company of Luttrell, Tennessee. The limestone is pulverized to a mmd of 80 μm and then injected through the burner with coal firing. Separation of the coarse sorbent particles is accomplished by extracting a sidestream of hot flue gas at the combustor outlet, cooling it, and passing it through a 40-ft^3/min (1.1-m^3/min) Fisher-Klosterman cyclone, as illustrated in Figure 3. The fly ash particles pass through the cyclone and are collected in a bag filter ahead of the side-stream, induced-draft (ID) fan. The sorbent particles collected in the cyclone are hydrated with 50 to 60% excess water in a 1-ft^3 (28.3-L) Ross ribbon blender. The hydrated sorbent is then injected back into the pilot combustor at a flue gas temperature of 2200°F (1200°C) as in the previous tests with the modified ash from hydrated lime injection.

Thus far, only preliminary tests have been carried out without the separation step (i.e., hydration and reinjection of the entire coarse sorbent/fly ash mixture). These tests were performed by reinjecting the modified ash into the combustor after collection and hydration. These tests yielded 48% sulfur capture at a Ca/S ratio of 2:1, based on available calcium. Again, this was comparable to the performance obtained with an equivalent amount of calcium in commercial hydrated lime. Work is now under way to demonstrate and optimize the separation of the coarse sorbent in the cyclone. A stream of bleed air is being used to vary the cyclone cutpoint, and the degree of separation is being assessed by analysis of the cyclone and bag filter catches.

Steam Elutriation

The last separation technique, steam elutriation, is still in an early stage of development. Preliminary results suggest that steam can be used to fluidize the modified ash and separate smaller particles by elutriation. However, only a small fraction of the free lime has been converted to $Ca(OH)_2$ in preliminary tests. The sulfate layer on the sorbent particles appears to greatly retard the rate of steam hydration, since reagent-grade CaO is fully hydrated under the same conditions. Steam hydration/elutriation tests are continuing using modified ash from both hydrated lime injection and coarse limestone injection.

CONCLUSIONS

Both the laboratory tests and the large-scale disposal study showed that the modified ash can be safely handled and landfilled. These studies showed that the cementitious reactions within the wetted ash can produce a nearly impermeable material, if the ash is properly conditioned and placed. With proper handling and conditioning, this should result in minimal potential for groundwater contamination from percolating leachates. Analyses of both EP leachates and runoff samples from the landfill test cell showed that all metal concentrations are well below RCRA limits. This is not surprising in view of the alkaline nature of this material and should prevent classification of this material as a hazardous waste under current RCRA specifications.

After an adequate period of stabilization (about 5 days in the test cell) the pH and solids content of the test cell sump were well within NPDES limits. However, a high-pH runoff was noted for several days after placement, before adequate setup had occurred. This may require monitoring and possibly neutralization of the runoff collected in the sump before it is discharged.

Adequate conditioning of the ash is a key factor in attaining optimum permeability characteristics. This should be monitored by periodic analyses of ash moisture content and measurements of in situ permeability. Ash haul trucks may be equipped with liners and vibrators to facilitate ash removal. Runoff neutralization, if needed, should be accomplished by addition of either acid or carbon dioxide. Depending on the extent of neutralization required, the latter might be accomplished with a conventional aerator since carbonation of the ash piles is due to atmospheric CO_2.

One of the most promising utilization concepts appears to be synthetic aggregate production for bituminous pavement applications. Production of the aggregate appears to be technically feasible using existing equipment, and conformance to highway department specifications appears to be possible. A systematic program of optimization, leading to a full-scale demonstration, appears to be justified.

One of the most promising recycle concepts appears to be the use of coarse limestone injection with cyclonic removal of the coarse calcine particles followed by hydration and reinjection. This effectively yields the performance of hydrated lime at the cost of coarse limestone, which is much less expensive. This concept should be demonstrated in pilot combustor tests, and an economic evaluation should be conducted.

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Table I. Modified fly ash analysis.

	Pittsburgh No. 8 coal and hydrated lime[a]	Ontario Hydro, Canada, high-sulfur coal and hydrated lime	Malmo, Sweden, Polish coal and hydrated lime
Sample Nos.	D-292-32,38,46,49	D-0753-7-3	D753-1-2
Loss on ignition, wt %	3.0	12.9	7.5
Elemental analysis,[b] wt %:			
Li_2O	0.01	0.02	0.05
Na_2O	0.12	0.45	1.0
K_2O	0.52	0.96	1.6
MgO	0.74	0.96	2.3
CaO	44.0	36.3	27.1
Fe_2O_3	8.8	10.5	6.9
Al_2O_3	7.3	14.8	20.0
SiO_2	14.2	28.5	32.0
TiO_2	0.5	0.58	1.1
P_2O_5	0.04	0.27	0.99
SO_3	21.6	6.4	6.7
Unaccounted for (by difference)	2.17	0.26	0.26

a. Simulated Edgewater modified ash from pilot combustor.

b. Analysis reported on ignited sample; all elements expressed as their oxides, but may occur in other forms.

Table II. Leachate data for simulated modified fly ash from SoRI combustor.

Metal	Concentration in extract, mg/L: Allowable limit per RCRA[a]	Concentration in extract, mg/L: Pittsburgh No. 8 coal and hydrated lime D292-46-5A
Arsenic	5	0.0145
Barium	100	4.11
Cadmium	1	0.00095
Chromium	5	0.0394
Lead	5	<0.0030
Mercury	0.2	<0.0003
Selenium	1	0.0296
Silver	5	<0.0005
pH	12.5	(12.4/12.2)[b]

a. Resource Conservation and Recovery Act, 41 CFR 35050, August 1976, enacted by Congress on October 21, 1976.

b. Before/after addition of 4 mL of 0.5 N acetic acid per 1 g of sample.

Table III. Permeability data for consolidated modified ash.

	Pittsburgh No.8 coal ash and spent hydrate D292-46-5B
Free base as CaO, wt %	25.10
Moisture content, wt %	28.5
Permeability, cm/sec:	
LIMB ash/water mix	
1-Day cure	2.75×10^{-4}
4-Day cure	1.90×10^{-4}
11-Day cure	4.35×10^{-5}
28-Day cure	5.80×10^{-6}
30-Day cure	3.65×10^{-6}
LIMB ash/water/cement mix	
28-Day cure	8.85×10^{-5}
30-Day cure	3.90×10^{-6}
Density, g/cc:	
LIMB ash/water mix	
1-Day cure	1.50
28-Day cure	1.56
LIMB ash/water/cement mix	
28-Day cure	1.58

Table IV. Wetting tests with Edgewater demonstration modified ash[a].

Water-to-free lime ratio, H_2O/CaO, mole/mole	Amount of water added: As percent of dry ash, %	Amount of water added: As percent of wet ash, %	Maximum adiabatic temperature, °F (°C)	Final product condition: From ribbon blender[b]	Final product condition: From KitchenAid mixer[c]
0.5	4.8	4.6	221 (105)	Dry powder	--
1	9.6	8.8	248 (120)	Dry powder	--
1.5	14.4	12.6	--	--	Dry powder
3	28.8	22.4	214 (101)	Dry with BB-sized clumps	--
4	38.4	27.7	--	--	Soil-like with BBs
5	48.0	32.4	199 (92.8)	Damp soil-like with BB- to marble-size clumps	
6	57.7	36.6	--	--	BB- to marble-size clumps
7	67.3	40.2	--	--	
8	76.9	43.5	151 (66.1)	Partly mud-like with later dry clumping	
9	86.5	46.4	--	--	Mortar-like
(12.4)[d]	119.6	54.5	143 (61.7)	Thick paste	--

a. All modified ash samples were produced from hydrated lime and Pittsburgh No. 8 coal fired in SoRI pilot combustor; free lime (CaO) content = 29% by weight.

b. Ribbon blender is a 1-ft^3 (28.3-L) Ross ribbon blender unit; all ribbon blender tests used 10 lb (4.5 kg) of modified ash with a mixing time of 4.5 min.

c. KitchenAid mixer tests used 200 to 800 g of modified ash with a mixing time of 4 min.

d. ASTM Slaking Test ASTM C-110.

Table V. Analysis of runoff samples from West Lorain landfill test cell[a].

Sample description						Sample analysis											
								Alkalinity as $CaCO_3$, mg/L		Concentration, mg/L							
Sample No.	Date	Time(am)	Location	Approx vol, mL		TSS, mg/L	pH	p	m	Arsenic	Barium	Cadmium	Chromium	Lead	Mercury	Selenium	Silver
D0753-10-4	7/28/86	11:10	SW	100													
D0753-11-6	7/28/86	11:06	NW	150	composite	230	12.0	--	--								
D0753-13-1	7/28/86	11:17	Sump	300		5.5	6.8	--	--	0.007	1.4	<0.0005	<0.005	<0.003	<0.001	<0.005	<0.0001
D0753-10-1	7/29/86	8:30	S	100													
D0753-11-11	7/29/86	8:30	N	100	composite	251	11.6	150	210	<0.002	7.1	<0.0005	0.014	<0.003	<0.001	<0.005	<0.0001
D0753-11-4	7/29/86	8:30	W	150													
D0753-12-1	7/29/86	8:30	Sump	300		17	7.1	--	-- [b]	<0.002	6.1	<0.0005	<0.005	<0.003	<0.001	<0.005	<0.0001
D0753-10-2	7/30/86	9:45	S	100													
D0753-9-7	7/30/86	9:45	ES	150	composite	300	11.4	54	80	0.004	7.4	<0.0005	0.027	<0.003	<0.001	<0.005	<0.0001
D0753-11-5	7/30/86	9:45	W	200													
D0753-13-2	7/30/86	9:45	Sump	300		22	7.2	--	74	0.006	1.8	<0.0005	<0.005	<0.003	<0.001	<0.005	<0.0001
D0753-10-3	7/31/86	9:15	S	100													
D0753-13-4	7/31/86	9:15	E	150	composite	885	11.5	162	193								
D0753-13-7	7/31/86	9:15	NNC	100													
D0753-12-2	7/31/86	9:15	Sump	300		6.9	7.2	--	89	0.005	2.2	<0.0005	<0.005	<0.003	<0.001	<0.005	<0.0001
D0753-11-8	8/2/86	10:30	NW	100		82	7.0	--	--								
D0753-9-4	8/2/86	10:05	Sump	150		8.4	7.2	--	--								
D0753-11-2	8/3/86	8:30	SW	100													
D0753-11-9	8/3/86	8:30	NW	150	composite	1620	6.9	--	--								
D0753-13-3	8/6/86	8:30	Sump	300		26	7.5	--	--	<0.002	2.6	<0.0005	<0.005	<0.003	<0.001	<0.005	<0.0001
D0753-8-6	8/19/86	--	S	135		156	7.6	--	66	0.009	14	0.0015	0.072	0.008	<0.001	<0.005	0.0007
D0753-8-7	8/19/86	--	Sump	100													
D0753-8-8	8/19/86	--	Sump	100	composite	8.5	7.7	--	92	0.003	2.1	<0.0005	<0.005	<0.003	<0.001	<0.005	<0.0001

a. The modified ash was placed in the test cell between 8:00 a.m. and 4:00 p.m. on July 24, 1986.

b. Not determined, sample inadvertently acidified after pH measurement.

Table VI. Results of Aardelite's tests on modified fly ash pellets.

Mixture	Pellet[a] No.	Pellet strength, psi (MPa)	Density, lb/ft^3 (g/cc)
80% Modified fly ash[b] 20% Water	1	10,780 (74.3)	90.00 (1.44)
40% Modified fly ash[b] 40% Holland fly ash 20% Water	9	4,775 (32.9)	88.13 (1.41)
40% Modified fly ash[b,c] 40% Holland fly ash[c] 20% Water	34	6,468 (44.6)	86.25 (1.38)
24% Modified fly ash[b] 32% Holland fly ash 24% Fine sand 20% Water	40	3,235 (22.3)	96.25 (1.54)

a. Forming pressure was 2,310 psi (15.9 MPa).

b. Modified fly ash from the Malmo plant in Sweden.

c. Preheated to 154°F (68°C).

Table VII. EP toxicity data for extracts from modified fly ash pellets.

Metal	Allowable extract level, mg/L[a]	Measured extract level, mg/L: IRD fine aggregate 57/43 mix[b]	IRD coarse aggregate 57/43 mix[b]	IRD asphalt plug	Aardelite pellet 80/20 mix[b]	SoRI pellet 80/20 mix[b] atmospheric steam cure	SoRI pellet 80/20 mix[b] room temp humidified atmosphere
Arsenic	5	0.0633	0.0454	0.0322	0.0386	0.0194	0.0088
Barium	100	1.3	1.2	1.1	1.2	<0.5	1.1
Cadmium	1	<0.0002	<0.0002	<0.0002	0.0003	0.0006	0.0006
Chromium	5	0.0053	0.0041	0.0073	0.0068	0.0234	0.0090
Lead	5	<0.0003	<0.0003	<0.0003	0.0051	0.0320	0.0111
Mercury	0.2	<0.0005	<0.0005	<0.0005	<0.0005	0.0058	0.0108
Selenium	1	<0.015	<0.015	<0.015	<0.015	0.0156	0.0344
Silver	5	<0.0005	<0.0005	<0.0005	<0.0005	0.0048	0.0022

a. Allowable levels according to RCRA.

b. Modified fly ash from Pittsburgh No.8 coal and hydrated lime.

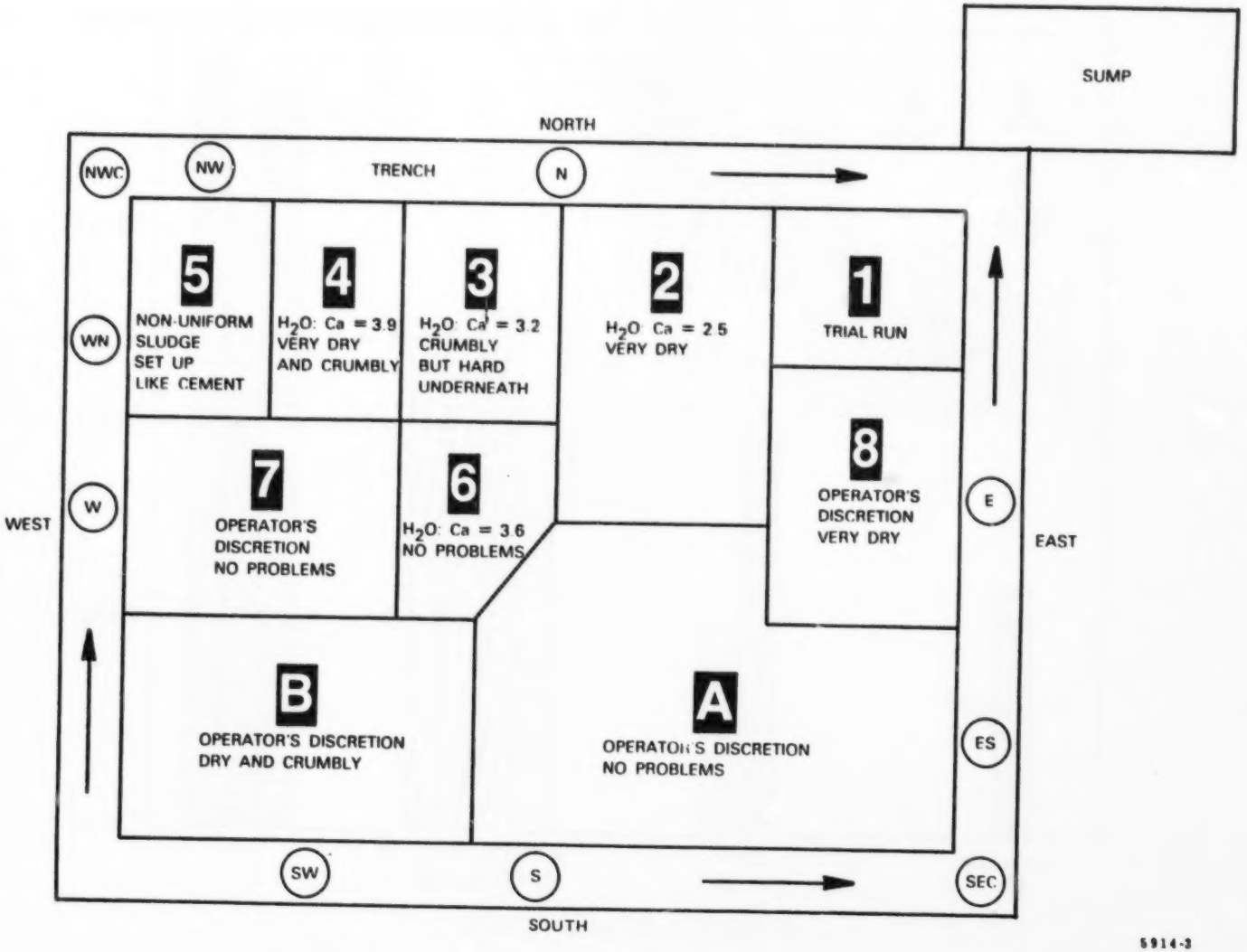

Figure 1. Locations of runoff samples taken at the West Lorain landfill test cell.

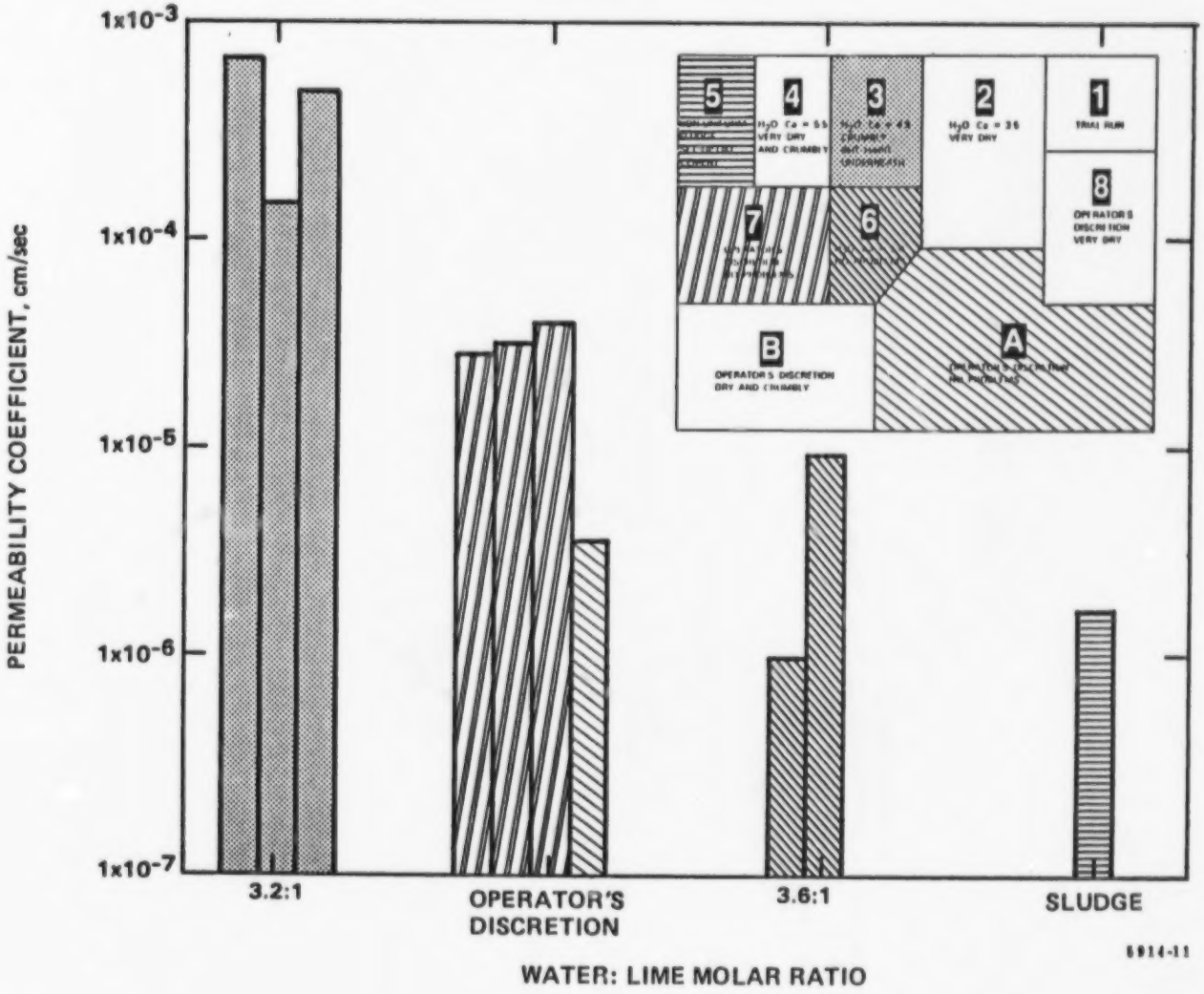

Figure 2. Permeability data from West Lorain test landfill.

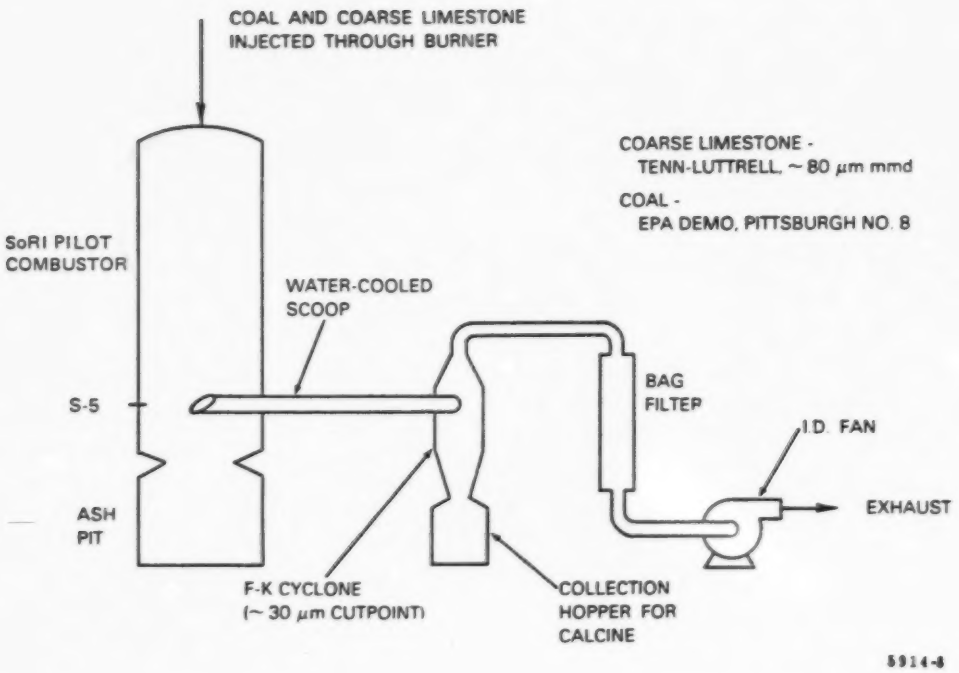

Figure 3. In situ cyclonic separation of coarse limestone calcine.